Thermal Properties and Raman Spectra of Crystalline and Vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$

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Differential thermal analysis and Raman spectroscopic studies have been performed of crystalline and vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds in order to examine the thermal properties and the F coordination of Zr. The differential thermal analyses clarified the definite phase transformation characteristics of crystalline $BaZrF_6$, and $SrZrF_6$ and also suggested that the low- and high-temperature modifications are present in $PbZrF_6$ as well as in $BaZrF_6$ and $SrZrF_6$. The Raman spectra of crystalline $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were discussed in relation to the F coordination of Zr in fluorozirconate compounds. The crystallization behaviors and Raman spectra of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ revealed that Zr in the vitreous compounds is eight-coordinated by F although small amounts of seven-coordinated Zr may exist in vitreous $BaZrF_6$.

Zirconiumtetrafluoride-based glasses recently developed[1)] are a new family of glasses and are noted in properties of high F ion conductivity and mid infrared transparency.[2)] Currently various properties of the glasses are being examined to evaluate the possibility of the potential applications.[2)] However, the structural studies are a few[3—5)] so that the glass structures are not thoroughly understood yet.

The binary systems BaF_2–, PbF_2–, and SrF_2–ZrF_4 yield vitreous materials in given composition ranges[6)] and besides the combination of the binaries and other fluorides gives a number of polynary fluorozirconate glasses.[2)] Accordingly the binary systems can be regarded as mother systems for fluorozirconate glasses. Thus, elucidating the structures of the binary glasses is indispensable for the structural understanding of ZrF_4-based fluoride glasses. As the first step of the structural studies of the BaF_2–, PbF_2–, and SrF_2–ZrF_4 glasses, the present authors dealt with Ba, Pb, and Sr metafluorozirconate glasses, that is, vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$.

The objective of this work is to elucidate the short-range structure, mainly the F coordination environment of Zr, of the vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$. Differential thermal analysis and Raman spectroscopy were employed for the investigation. A method frequently employed for inferring the structure of a glass is to compare the various spectra of the glass with those of the related crystalline compounds. In the present study the thermal properties and Raman spectra of crystalline $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ that were not reported were first studied. Then the thermal behaviors and Raman spectra of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were examined and compared with those of the crystalline compounds.

Experimental

Materials. Raw materials employed for the preparation of crystalline and vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were ZrF_4 (Morita Chemicals, 99.9% purity), BaF_2(Merck, suprapur), PbF_2 (Merck, suprapur), and SrF_2(Merck, suprapur). About 5 g stoichiometric mixtures of the raw materials with addition of small amounts of NH_4HF_2 were melted in platinum crucibles in an N_2 gas atmosphere using a simple SiC resistance furnace and the melts were kept at about 850 °C for 10 min. The low-temperature modifications(α) of $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were obtained by cooling the melts slowly to room temperature in the furnace. On the other hand, the high-temperature forms(β) of $BaZrF_6$ and $SrZrF_6$ were prepared by crystallizing the melts at temperatures a few degrees below their melting points and then quenching them by liquid nitrogen. Vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were prepared by quenching the melts rapidly using a twin roller. The synthesized crystalline compounds were polycrystalline and were identified by X-ray powder diffraction to be the respective single phases. In the identification the reference X-ray powder patterns were computed from the available crystal structure data. The prepared vitreous compounds were thin films of about 20 μm thickness and amorphous in X-ray diffraction.

Differential Thermal Analyses. Differential thermal analyses were undertaken to examine the phase transformation (T_t) and melting (T_m) temperatures of crystalline $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds and the glass transition(T_g) and crystallization (T_c) temperatures of the vitreous compounds. The measurements were made in an Ar gas stream with a heating or cooling rate of 5 °C min^{-1}.

Raman Spectra. Raman scattering of crystalline and vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were measured with a Spex 14018 double monochromator in the 90° scattering configuration using the Ar^+ 488.0 nm laser line at ambient temperature. In the measurements the slits were opened to 400 μm and the pressed-disc samples were used. No sample deterioration was observed under irradiation with an about 150 mW beam.

Results and Discussion

Differential Thermal Analyses. So far the followings have been reported on the modifications and crystal structures of $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$: Both $BaZrF_6$ and $SrZrF_6$ have the low- and high-temperature modifications but $PbZrF_6$ is present only in a single modification.[7)] The structures of β-$BaZrF_6$, $PbZrF_6$, and α-$SrZrF_6$ are crystallographically isomorphous and are composed of $(ZrF_8)^{4-}$ dodecahedra connected by two edges to form chain linked by Ba^{2+}, Pb^{2+}, and Sr^{2+} ions.[7)] The structure of α-$BaZrF_6$ is built up of $(Zr_2F_{12})^{4-}$ complex anions linked by Ba^{2+} cations, where a Zr atom is coordinated by seven F atoms.[8)]

Although the presence of α- and β-modifications in $BaZrF_6$ and $SrZrF_6$ is confirmed in crystal structure studies the α-β phase transformation temperatures are not well-defined. Furthermore, even the melting temperatures of $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ are not reported. In the present work, therefore, thermal studies were first made of crystalline $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds with differential thermal analysis. In the analyses the products at endotherm or exotherm peaks were identified by X-ray diffraction measurements of the quenched samples. The results of α- and β-$BaZrF_6$, $PbZrF_6$, and α- and β-$SrZrF_6$ are shown in Figs. 1(a, b), 2(a), and 3(a, b), respectively, where

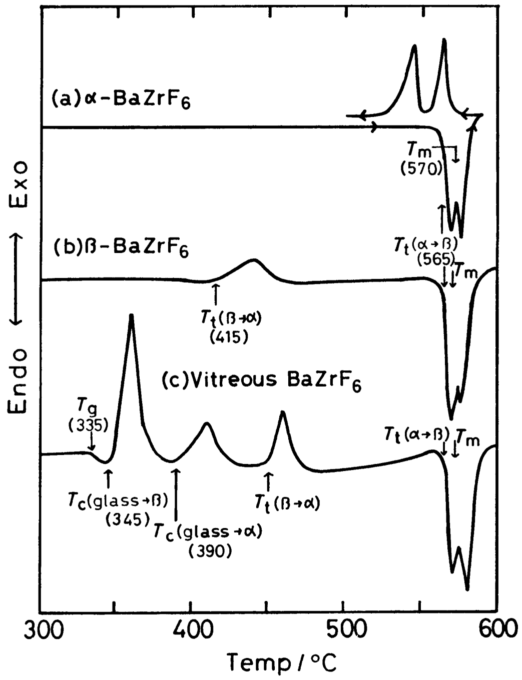

Fig. 1. Differential thermal analysis curves of α- and β-$BaZrF_6$ and vitreous $BaZrF_6$. Numerals in parentheses are temperatures in °C.

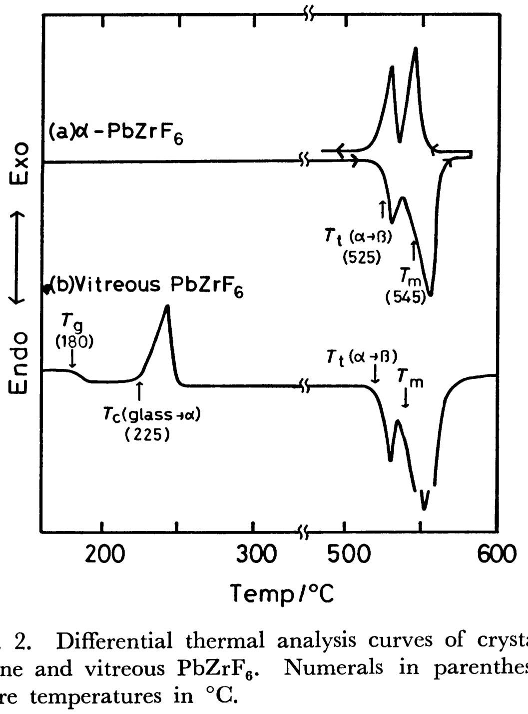

Fig. 2. Differential thermal analysis curves of crystalline and vitreous $PbZrF_6$. Numerals in parentheses are temperatures in °C.

the subscripts ($\alpha\rightarrow\beta$) and ($\beta\rightarrow\alpha$) of T_t refer to transformation from α-form to β-form and from β-form to α-form, respectively. As shown in Figs. 1(a, b) and 3(a, b), the phase transformation characteristics of $BaZrF_6$ and $SrZrF_6$ were clearly defined. As can be seen from Fig. 2(a), on the other hand, $PbZrF_6$ showed a differential thermal analysis curve very similar to those of α-$BaZrF_6$ and α-$SrZrF_6$. This indicates that $PbZrF_6$ also may exhibit the α-β phase transformation and that crystalline $PbZrF_6$ already known may be the α-modification. The attempt of preparing β-$PbZrF_6$ according to the method described in Experimental was unfortunately unsuccessful. So the presence of α- and β-modifications in $PbZrF_6$ could not be firmly established in this work.

The differential thermal analysis curves of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds are shown in Figs. 1(c), 2(b), and 3(c), respectively, where the subscripts (glass$\rightarrow\alpha$) and (glass$\rightarrow\beta$) of T_c indicate that α- and β-form compounds crystallized from glasses, respectively. The crystallization behaviors show that the crystallized products of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ were β-$BaZrF_6$ and small amounts of α-$BaZrF_6$, α-$PbZrF_6$, and α-$SrZrF_6$, respectively.

Raman Spectra. The Raman spectra observed for crystalline $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds are shown in Figs. 4—6. In the figures the Raman peaks with asterisks may be bands assigned to symmetric stretching vibration (ν_s).

Here the Raman spectra of crystalline fluorozirconates are discussed in relation to the F coordination of Zr. It is known that, in crystalline fluorozirconates, Zr atoms exhibit three kinds of F coordination numbers (six, seven, and eight) to form fluorozirconate complex anions. Toth *et al.* measured the Raman spectra of

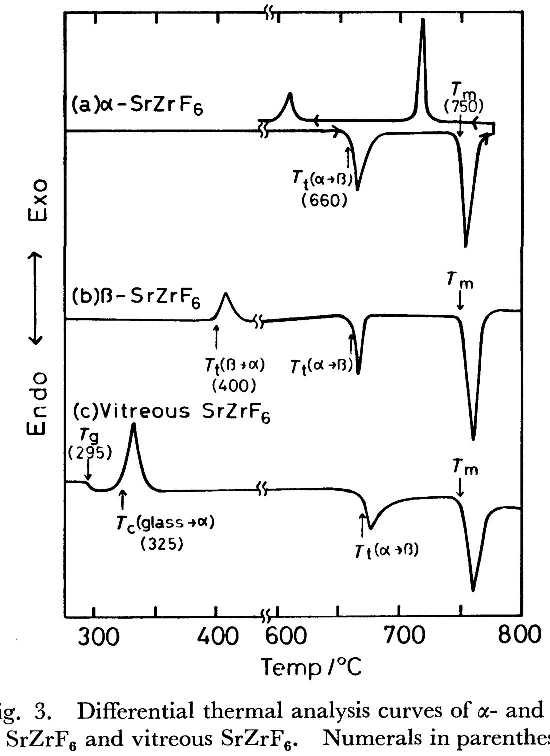

Fig. 3. Differential thermal analysis curves of α- and β-$SrZrF_6$ and vitreous $SrZrF_6$. Numerals in parentheses are temperatures in °C.

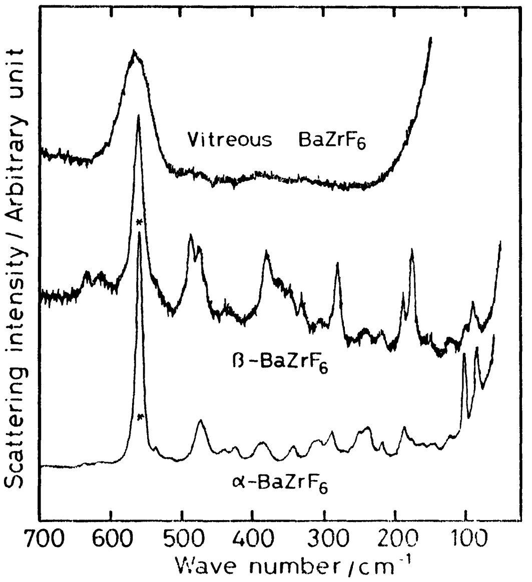

Fig. 4. Raman spectra of α- and β-$BaZrF_6$ and vitreous $BaZrF_6$.

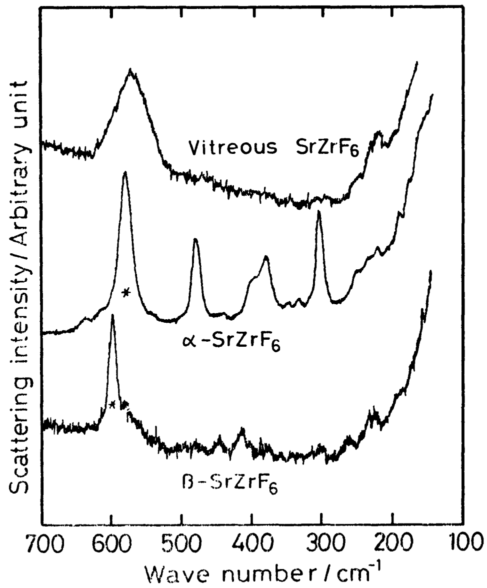

Fig. 6. Raman spectra of α- and β-$SrZrF_6$ and vitreous $SrZrF_6$.

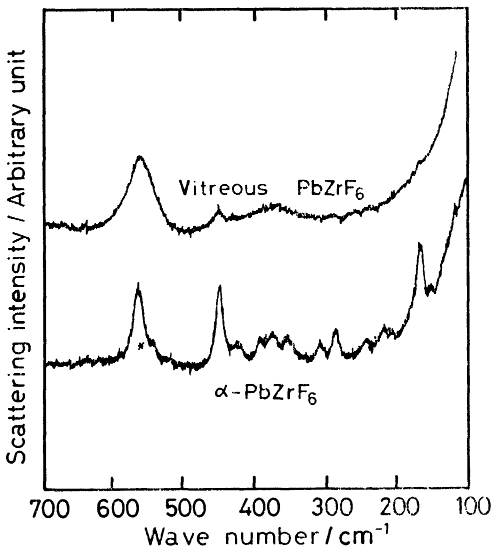

Fig. 5. Raman spectra of crystalline and vitreous $PbZrF_6$.

several alkali fluorozirconate compounds with known crystal structures and discussed the correlation between the ν_s and the F coordination number of Zr.[9] They mentioned that, only in the absence of bridging between F complex ions of Zr, an inverse correlation between the ν_s and the coordination number holds.

The ν_s frequencies observed for the present compounds and alkali fluorozirconate compounds are classified according to the F coordination number of Zr and tabulated in Table 1. In the table the average Zr–F bond lengths and structural characteristics in the respective compounds are also given. In the series of alkali fluorozirconates an inverse correlation is found between the ν_s and the F coordination number, but throughout alkali and alkaline earth fluorozirconates such a correlation does not hold at all. In particular the Zr atoms in β-$BaZrF_6$, α-$PbZrF_6$, and α-$SrZrF_6$ have the same F coordination number(eight) and the same dodecahedral coordination.[7] Nevertheless the ν_s frequencies in the three compounds are significantly different from each other, though the ν_s frequency differences might be probably attributed to the Badger rule, *i.e.*, an inverse correlation between ν_s and Zr–F bond length.[15] The same situation can be seen in a set of Li_2ZrF_6 and Cs_2ZrF_6. Thus no consistent correlation can be deduced between the ν_s and the F coordination number of Zr in fluorozirconate compounds. The following reasons for this may be supposed: Even if the F coordination number is identical the coordination environment may be highly different, especially in large coordination numbers. Moreover, when bridging takes place between the F complex ions it should give many complicated effects on the ν_s vibrations. The bridging manner also may be different in the respective compounds. The above concludes that the Raman ν_s frequency can not be utilized as a reliable guide for identifying the F coordination number of Zr in a fluorozirconate complex with unknown structure.

F Coordination Numbers of Zr in Vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$. The Raman spectra of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ are shown in Figs. 4, 5, and 6, respectively, together with those of the corresponding crystalline compounds to facilitate the comparison between both the spectra. In the vitreous Raman spectra only the polarized bands were strong and prominent, and all other bands were very weak and broad. In a comparison of vitreous spectra and crystalline spectra, very close resemblance in spectral features can be seen between vitreous $BaZrF_6$ and β-$BaZrF_6$, between vitreous $PbZrF_6$ and α-$PbZrF_6$, and between vitreous $SrZrF_6$ and α-$SrZrF_6$. As already described, on the other hand, the crystallization products of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ compounds were predominantly β-$BaZrF_6$, only α-$PbZrF_6$, and only α-$SrZrF_6$, respectively. In general it is antic-

TABLE 1. F COORDINATION NUMBERS OF Zr AND RAMAN ν_s FREQUENCIES IN VARIOUS FLUOROZIRCONATE COMPOUNDS

Coordination number	Compound	ν_s/cm^{-1}	Average Zr-F bond length/nm	Structural characteristics	Ref.
8	β-$BaZrF_6$	562	0.2138	Edge-shared $(ZrF_8)^{4-}$ chain[a]	7
	α-$PbZrF_6$	567	0.2095	Edge-shared $(ZrF_8)^{4-}$ chain[a]	7
	α-$SrZrF_6$	578	0.2080	Edge-shared $(ZrF_8)^{4-}$ chain[a]	7
	K_2ZrF_6	525[c]	0.2112	Edge-shared $(ZrF_8)^{4-}$ chain	10
	$Na_7Zr_6F_{31}$	548[c]	0.2113	Bridged $(ZrF_8)^{4-}$ complex	11
7	α-$BaZrF_6$	560	0.2082	Edge-shared $(ZrF_7)^{3-}$ dimer	8
	Na_3ZrF_7	556[c]	0.2280	Free $(ZrF_7)^{3-}$ ion	12
6	Cs_2ZrF_6	577[c]	0.2035	Free $(ZrF_6)^{2-}$ ion[b]	13
	Li_2ZrF_6	585[c]	0.2016	Free $(ZrF_6)^{2-}$ ion[b]	14
?	β-$SrZrF_6$	598	?	?	

a) Isostructural ZrF_8 dodecahedron. b) Isostructural ZrF_6 octahedron. c) Ref. 9.

ipated that compounds which crystallize from a glass are crystals with the structures closer to the glass structures. Therefore the crystallization behaviors and Raman spectra of vitreous $BaZrF_6$, $PbZrF_6$, and $SrZrF_6$ conclude that the Zr atoms in the vitreous compounds are eight-coordinated by the F atoms like the Zr atoms in crystalline β-$BaZrF_6$, α-$PbZrF_6$, and α-$SrZrF_6$. Furthermore it may be proposed that the basic structures of the vitreous compounds consist of chains of ZrF_8 dodecahedra. Radial distribution analyses of the vitreous $BaZrF_6$ and $PbZrF_6$ compounds are now in progress to verify the present proposal.[16] Here it is a wonder that vitreous $BaZrF_6$ has a $\underline{\beta}$-$BaZrF_6$-like structure and, on the contrary, vitreous $PbZrF_6$ and $SrZrF_6$ possess the $\underline{\alpha}$-form crystal-like structures. Elucidating the crystal structures of β-$PbZrF_6$ and β-$SrZrF_6$ should answer to this question.

Almeida and Mackenzie have inferred that the Ba metafluorozirconate glass is composed of six- and seven-coordinated Zr atoms.[3] In their study, however, they have compared the Raman spectra of fluorozirconate glasses with those of alkali fluorozirconate compounds. This comparison is not proper, as described in the preceding section. In addition it is questioned that the crystallized product of the glass has been reported to be α-$BaZrF_6$. Probably the product identified by Almeida and Mackenzie would be the phase-transformed product of β-$BaZrF_6$ that crystallized initially from the glass.

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